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STRUCTURE OF MATTER AND QUANTUM CHEMISTRY

Solvatochromism of Vibronic Components of the 1B_g Absorption Band of Anthracene Solution and Melt at 500 K

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Abstract – The modern semiempirical theory of solvatochromism was first applied in order to interpret the general behavior of the solvation shift of the vibronic 0–0 component (corresponding to electronic transition in the intense 1B_g absorption band of anthracene) upon gas–solution–melt phase transition at 500 K. Using our approach, which was developed on the basis of dispersion of the effective field, we determined the parameters of various shift components attributed to different intermolecular forces. The experimental results were shown to correlate with the theory. It is confirmed that analyzing solvatochromic properties of the individual components of a vibronic band in high intensity spectra, instead of those of the envelope of this band, is of particular importance for improving the accuracy and reliability of the results.

Recently, experimental data characterizing not only the solvent-induced shift of the envelope of complex vibronic bands but also the spectral shifts of individual vibronic components of the band, have been extensively used in analyzing solvatochromic dependences. This trend is well justified if we consider that the key relationships of the modern semiempirical theory of solvatochromism describe, strictly speaking, the frequency shift of purely electronic transition in the absorption and emission spectra (see, for example, [1, 2]), whereas, in practice shifts, of the maximum of the spectral band envelope are usually measured. This suggests that an analysis of solvatochromic properties of individual vibronic components of electronic bands, rather than those of their envelope, permits one to obtain more comprehensive and precise information about the solvent effect on the optical spectra of molecules and to increase the accuracy and reliability of theoretical interpretations of the results.

The above-mentioned situation can be illustrated by the data presented in [3, 4]. References [3, 4] contain numerous experimental data on the spectroscopic characteristics (position, intensity, and shape) of several vibronic components of the anthracene 1B_g band in the observed absorption spectra $\kappa(\nu)$ and spectra of the Einstein absorption coefficient $B(\nu)$ for several solutions at room temperature.

Taking into account the fundamental importance of the obtained results to modern molecular spectroscopy of the condensed state, we believe that continuation of the investigations started in [3, 4] (see also [5, 6]) is of substantial interest. This work is the first attempt to apply the concepts and relationships of the semiempirical theory of solvatochromism [1, 2] to the quantitative interpretation of the changes in the shift of the vibronic component pertaining to the electronic transi-

tion in the intense 1B_g band of anthracene induced by the gas–solution–melt phase transition at 500 K. To solve the above problem we used the results obtained in [7], which allow us to calculate by analogy with [3, 4] various constituents of the solvation shift of the vibronic component from the experimental data [8]. We recall that, by the definition, the experimentally measured spectral shift of the band caused by a solvent can be written:

$$\Delta\nu_{0i}^c = \nu_{0i}^s - \nu_{0i}^g, \quad (1)$$

where ν_{0i}^s and ν_{0i}^g are the frequencies of the 0– i vibronic component maxima in the $\kappa(\nu)$ spectra of the solution (melt) and gas. Then, according to [1, 2]

$$\Delta\nu_{0i}^c = \Delta\nu_{0i}^{c(\text{dyn})} + \Delta\nu_{0i}^{c(\text{stat})}, \quad (2)$$

with

$$\Delta\nu_{0i}^{c(\text{dyn})} = \nu_{0i}^s - \nu_{0i}^B, \quad (3)$$

$$\Delta\nu_{0i}^{c(\text{stat})} = \nu_{0i}^B - \nu_{0i}^g, \quad (4)$$

where $\Delta\nu_{0i}^{c(\text{dyn})}$ and $\Delta\nu_{0i}^{c(\text{stat})}$ are the components of the solvation shift determined by the dynamic and static intermolecular forces [2 - 4], and ν_{0i}^B is the frequency corresponding to the 0– i component maximum in the spectrum of the Einstein coefficient $B(\nu)$ of the solution or melt.

Table 1 presents the frequencies [7] of the maxima of 0–0, 0–1, and 0–2 vibronic components of the 1B_g anthracene band in the $\kappa(\nu)$ spectra of all the investigated systems (including gaseous phase). Table 1 also lists the frequencies corresponding to the maximum of the vibronic band envelope (ν_Σ^c) and the solvation shifts of the maxima of the envelope and the vibronic components. An analysis of this data confirms the basic results

Table 1. Position (ν_{Σ}^{κ} , ν_{0i}^{κ}) and solvation shift ($\Delta\nu_{\Sigma}$ and $\Delta\nu_{0i}$) of the maxima of the envelope and vibronic components of the 1B_g absorption band in anthracene $\kappa(\nu)$ spectra (cm^{-1})

State	T, K	ν_{Σ}^{κ}	ν_{00}^{κ}	ν_{01}^{κ}	ν_{02}^{κ}	$-\Delta\nu_{\Sigma}$	$-\Delta\nu_{00}$	$-\Delta\nu_{01}$	$-\Delta\nu_{02}$
Gas	—	42200	40950	42270	43550	—	—	—	—
Solution in decane	300	39500	39500	40530	41760	2700	1450	1740	1790
Solution in decane	500	39950	39950	41150	42450	2250	1000	1120	1100
Melt	500	38450	38450	39650	40950	3750	2500	2620	2600

obtained in [3]. Thus, the shifts of the vibronic components were again found to be considerably less (approximately by a factor of 1.5 or 2) than the corresponding shifts of the envelope maximum. Moreover, a regularity, according to which the solvation shift of the 0-0 component differs from that of the 0-1 and 0-2 components, is reproduced; at 500 K this difference is much less than that at room temperature. This behavior is apparently due to the fact that at elevated temperatures dispersion of the effective light-wave field, caused by intermolecular interactions [of resonance (melt) or inductive-resonance nature (solution)], influences the contour and, hence, the vibrational structure of the investigated vibronic band to a lesser degree than it does at 300 K. This is primarily confirmed by the general reduction of the solvatochromic effect with increasing temperature showing up as a shorter wave shift of all the bands and also by a significant temperature broadening of both the envelope and each vibronic component [3].

Taking into account that, contrary to the envelope maximum, spectral shifts of the band adequately characterize the rearrangement of the entire system of vibronic transitions (see Table 1), we propose to make a direct quantitative comparison of the theoretical relationships that govern the solvatochromic effects exerted on the band of the 0-0 vibronic component with the experimental data. Table 2 presents the frequencies, borrowed from [7], of band maxima of the 0-0 component in the $\kappa(\nu)$ and $B(\nu)$ spectra of all the systems investigated and the parameters of various components of their solvation shift, determined by formulas (1) - (4). Dynamic (resonance and inductive-resonance) components were theoretically estimated by the known relationship [2, 9, 10]

$$\Delta\nu_{\text{dyn}}^{\text{calc}} = -\frac{he^2f}{4\pi^2mva^3} \frac{n^2 - 1}{2n^2 + 1}, \quad (5)$$

where e and m are the charge and mass of the electron; f and ν are the oscillator strength and frequency of the spectral band maximum; a is the effective radius of interaction (Onsager radius of a solute molecule); and n is the refractive index n_d of the solvent (dilute solution) or background refractive index of the liquid n_b (melt).

As is well known, in describing static intermolecular interactions in nonpolar solutions such as

anthracene, one should account for repulsive and attractive dispersion forces. According to [2, 3, 11], the general expression for a static component of the solvation shift is:

$$\Delta\nu_{\text{stat}}^{\text{calc}} = \Delta\nu_{\text{rep}}^{\text{calc}} + \Delta\nu_{\text{disp}}^{\text{calc}}, \quad (6)$$

where

$$\Delta\nu_{\text{rep}}^{\text{calc}} \approx \frac{2}{3} \frac{\alpha_e}{a^3} \left(1 - \frac{\alpha_g}{\alpha_e}\right) f(n), \quad (7)$$

$$\Delta\nu_{\text{disp}}^{\text{calc}} \approx \frac{(\alpha_g - \alpha_e)}{a^3} f(n), \quad (8)$$

with

$$f(n) = \left(\frac{3}{2} \frac{II_s}{I + I_s} \right) \frac{n^2 - 1}{n^2 + 2}. \quad (9)$$

Here, α_g and α_e are polarizabilities of dissolved molecules in the ground and in excited states, I and I_s are the first ionization potentials of interacting molecules (index "s" signifies solvent molecules). Based on the above-mentioned information, the meaning of the other quantities is clear. Note, that for a single-component liquid (melt), formula (9) can be written as

$$f(n) = \frac{3}{4} I \frac{n_b^2 - 1}{n_b^2 + 2}, \quad (10)$$

where n_b is the background refractive index of the melt mentioned above.

Table 2 presents various components of the solvation shift for the 0-0 vibronic component calculated from (5) to (10) of the absorption band. As mentioned above, the accuracy of these calculations does not exceed 20 - 30%. We used the following values of the molecular parameters of investigated systems [12]: $\alpha_g = 26 \text{ \AA}^3$, $\alpha_e \approx 70 \text{ \AA}^3$, $a = 6.0 \text{ \AA}$; $I = 7.4 \text{ eV}$; $I_s \approx 10 \text{ eV}$. The oscillator strength f of the 1B_g band was set at 4.5 [6] for the solution in decane at 300 K and at about 5 for the solution and melt at 500 K. The refractive index of decane at 500 K estimated from the refractometric and densitometric data was 1.32. The background refractive index of liquid anthracene at 500 K is close to 1.53.

An analysis of the data from Table 2 shows that the calculated and experimental parameters agree, i.e., the calculations provide a full quantitative interpretation of

Table 2. Experimental (Δv_{00}^e) and calculated (Δv_{00}^{calc}) components of the solvation shift of the 0-0 vibronic component in the anthracene 1B_u absorption band (cm^{-1})

State	T, K	v_{00}^e	v_{00}^B	$-\Delta v_{00}^e (\text{dyn})$	$-\Delta v_{00}^e (\text{stat})$	$-\Delta v_{00}^e$	$-\Delta v_{00}^{calc} (\text{dyn})$	$-\Delta v_{00}^{calc} (\text{disp})$	$\Delta v_{00}^{calc} (\text{rep})$	$-\Delta v_{00}^{calc} (\text{stat})$	$-\Delta v_{00}^{calc}$
Gas	—	40950	40950	—	—	—	—	—	—	—	—
Solution in decane	300	39500	40010	510	940	1450	740	2600	1700	900	1640
Solution in decane	500	39950	40480	530	470	1000	730	2000	1400	600	1330
Melt	500	38450	40200	1750	750	2500	1200	2800	1800	1000	2200

the solvatochromic data presented in [7]. In this case, the theory not only correctly predicts all the main peculiarities of the photophysical phenomenon considered (including such a fine effect as temperature shift in the solution spectra) but also enables one to explain the mechanisms of solvation processes responsible for spectroscopic observed effects. It is significant that the solvation shift parameters of the vibronic band envelope, as follows from Tables 1 and 2, correlate with theoretical estimates to a considerably lesser extent than do the appropriate data for the individual vibronic components.

Hence, results of our investigation demonstrate that the semiempirical theory of solvatochromic (solvato-fluorochromic) phenomena and the above-mentioned concepts upon which it is based enable us to interpret not only the full body of experimental data for anthracene solutions in various solvents at room temperature [3, 4] but more complicated spectroscopic phenomena observed within a wide temperature range during gas-solution-melt phase transition [7, 8] as well. This confirms that an analysis of solvation shifts of the individual vibronic band components (in the first place, 0-0 transition) in investigations of solvatochromism of intense vibronic absorption and emission spectra is more important than studies of the shift band envelope. This in turn necessitates comparative vibrational analysis of the experimental $\kappa(\nu)$ and Einstein coefficient $B(\nu)$ spectra, an analysis that becomes a mandatory stage for examining solvatochromic prop-

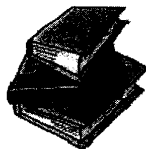
erties and increases the accuracy and reliability of the data obtained.

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